

RESOLVING ORTHOCLASE DISSOLUTION PROCESSES

The process by which feldspars (e.g. orthoclase) weather has been the subject of intense research and has important implications. We have studied the chemical weathering of orthoclase through direct Angstrom-scale measurements using *in situ* x-ray reflectivity at the Advanced Photon Source and atomic force microscopy as a function of pH and temperature. These observations clarify differences in orthoclase dissolution mechanisms as a function of pH and place new constraints on the understanding of alkali feldspar weathering processes. We have distinguished the separate roles of steps/defects vs terraces in orthoclase dissolution at different pH conditions.

How do minerals weather? Weathering is commonly observed as the degradation of monuments and historic buildings. Weathering is an important low-temperature geochemical process that involves both physical (e.g., abrasion) and chemical (e.g., dissolution) processes. Feldspars having typical end-member compositions of $\text{K}[\text{AlSi}_3\text{O}_8]$, $\text{Na}[\text{AlSi}_3\text{O}_8]$, and $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ are the most common crystal minerals and consist of 6 of the 8 most abundant elements in Earth's crust. Feldspar weathering influences global cycling of Si, Al, and alkali and alkaline earth metals; atmospheric CO_2 concentration; natural water composition; and soil formation [1].

The current understanding of feldspar weathering has been developed from studies of the pH-dependent dissolution behavior of individual feldspar minerals. The mechanisms of feldspar-water interfacial reactions are inferred to be different at acidic and alkaline pH on the basis of the pH and temperature dependence of dissolution kinetics and differences in the reaction stoichiometry. Despite the extensive investigation of this subject in the past several decades, the dissolution mechanisms remain controversial (see review by Blum and Stillings [2] and references therein), and a number of fundamental issues have yet to be properly resolved. For instance: Why is dissolution nonstoichiometric at acidic pH and stoichiometric at alkaline pH (near room temperature)? What is the nature of the nonstoichiometric layers? What are the relative reactivities of the different sites exposed at a feldspar mineral surface?

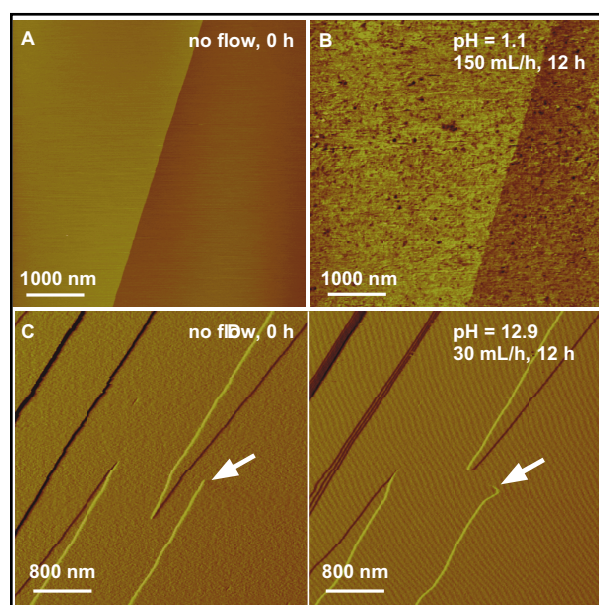


FIG. 1. AFM images of the change in orthoclase surface morphology during reaction. Images of the freshly cleaved surface and the same area after reaction for 12 hr are shown at pH 1.1 (a-b) and pH 12.9 (c-d). A screw dislocation is noted by an arrow in c and d. Adapted from Ref. 3.

Direct measurements of the Ångström-scale dissolution process were made by using *in situ* atomic force microscopy (AFM) and synchrotron x-ray reflectivity as a function of pH and temperature to provide unambiguous constraints on the dissolution process (for experimental details, see Ref. 3). We studied the (001) cleavage surface of orthoclase, $\text{K}[\text{AlSi}_3\text{O}_8]$, which in previous studies has been demonstrated to be molecularly flat [4]. AFM results

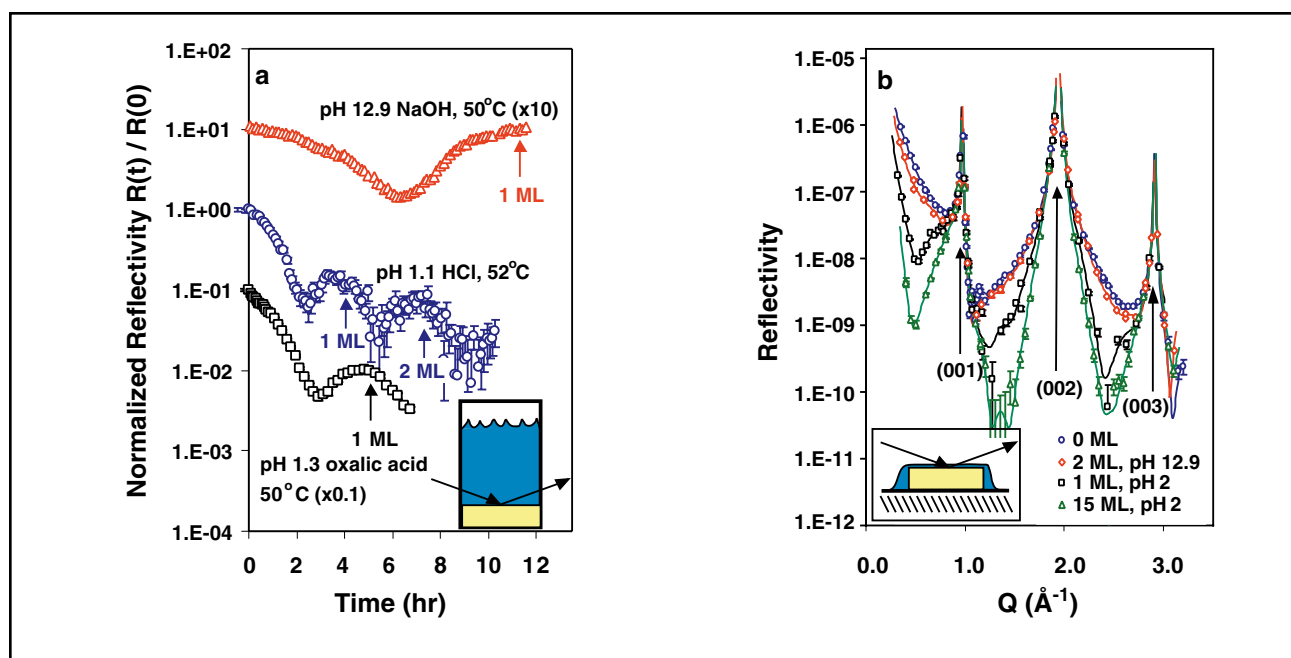


Fig. 2. (a) *In situ* x-ray reflectivity versus time (measured at $Q = 0.48 \text{ \AA}^{-1}$) during reaction at pH 1.1 (HCl), pH = 1.3 (oxalic acid), and pH 12.9 (NaOH). The removal of successive monolayers (MLs) is noted for each set of data. (b) CTR profiles for the freshly cleaved surface (circles) and surfaces reacted at pH 2.0 (1 and 15 ML dissolved) and pH 12.9 (2 ML dissolved). CTR profiles were measured in deionized water at room temperature ($T = 25 \pm 2^\circ\text{C}$). Schematics of the sample cells are shown in inset. Adapted from Ref. 3.

reveal distinct processes involving mainly terrace roughening and pitting with no significant step reactivity at pH 1.1 (Figs. 1a and 1b), versus step motion with little reactivity on terrace areas at pH 12.9 (Figs. 1c and 1d). This observation immediately implies that the reactive sites are pH-dependent. Separate measurements showed that a gel-like surface coating formed at acidic pH when slow fluid flow rates were used. This coating could be removed by increasing the flow rate. No coating was observed at alkaline pH for any flow rate or at acidic pH under high fluid flow rates. Therefore, we conclude that the widely observed nonstoichiometry of reaction is not a result of differential leaching of mineral components but instead is due to the deposition of a weakly bound film consisting of the less soluble reaction products.

Real-time x-ray reflectivity data obtained *in situ* during dissolution are shown in Fig. 2a. The measured x-ray reflectivity did not decrease monotonically with time during dissolution, as would be characteristic of random dissolution (e.g., where all exposed tetrahedral sites dissolve at the same rate).

Instead, the reflectivity exhibited an oscillatory pattern at both acidic and alkaline pH values. This observation implies that two distinct reactive sites (e.g., terrace and step sites) are found on the surface in each pH regime [3]. The full recovery of the reflectivity at pH 12.9 upon dissolution of the first layer implies that dissolution at alkaline pH is fully stoichiometric and dominated by lateral dissolution processes producing layer-by-layer dissolution. At pH 1.1 we observed a very different damped oscillatory pattern, indicative of a more random dissolution process in which the orthoclase surface is substantially disrupted and roughened.

We also obtained “snapshots” of the dissolution process through high-resolution x-ray reflectivity measurements of previously reacted surfaces (Fig. 2b). Crystal truncation rod (CTR) data were obtained for a freshly cleaved orthoclase surface, after dissolution of approximately 1 and 15 monolayers (MLs) at pH 2.0, and after dissolution of 2 monolayers at pH 12.9 (1 monolayer = $5.7 \times 10^{-10} \text{ mol cm}^{-2}$). All CTR measurements were performed in deionized water in a “thin-

film” cell (Fig. 2b, inset). The acid-reacted surfaces showed substantial changes in surface termination, including step proliferation and local etching described by an error function profile of the atomic occupation factors that is nonstoichiometric in only the outermost unit cell. In contrast, the alkaline-reacted sample showed no evidence of local terrace etching (consistent with the AFM images) and only a small increase in the surface step density.

These observations clarify differences in orthoclase dissolution mechanisms as a function of pH and place new constraints on the understanding of alkali feldspar weathering processes. We have distinguished the separate roles of steps/defects versus terraces in orthoclase dissolution at different pH conditions, providing direct evidence for distinct elementary dissolution reactions and reaction sites [3]. By probing the systematic variation of absolute dissolution rates as a function of pH, temperature, solution composition, cleavage plane, and feldspar mineral phase, we expect to gain a fundamental understanding of these molecular-scale dissolution and weathering processes.

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P. Fenter,¹ H. H. Teng,² L. Cheng,¹ N. C. Sturchio³

¹ *Environmental Research Division, Argonne National Laboratory, Argonne, IL, U.S.A.*

² *Department of Earth and Environmental Sciences, The George Washington University, Washington, DC, U.S.A.*

³ *Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL, U.S.A.*